RISM 3D (Following JCP 107, 6400)

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0.1 Molecular ensemble averages

Angle dependent pair distribution function is defined as:

$$\rho^{(2)}(\boldsymbol{r}^2, \boldsymbol{\omega}^2) = N(N-1) \int \frac{e^{-\beta U(\boldsymbol{r}^N, \boldsymbol{\omega}^N)}}{Z_C} d\boldsymbol{r}^{N-2} d\boldsymbol{\omega}^{N-2} \tag{1}$$

In the angular-dependent case, the normalization is given as:

$$\int \rho^{(1)}(\boldsymbol{r}, \boldsymbol{\omega}) d\boldsymbol{r} d\boldsymbol{\omega} = N \tag{2}$$

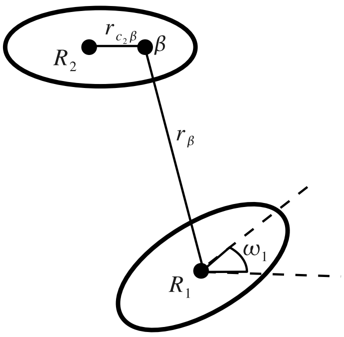
For the uniform case $\rho^{(1)} = C$ and

$$\int C d\boldsymbol{r} d\boldsymbol{\omega} = CV\Omega = N \Rightarrow C = \frac{\rho}{\Omega} \tag{3}$$

where $\Omega = \int d\omega$ (as i understand $\Omega = 4\pi^3$)

The pair distribution function is connected to the molecule correlation function:

$$\rho^{(2)}(\boldsymbol{r}^2, \boldsymbol{\omega}^2) = \left(\frac{\rho}{\Omega}\right)^2 g(\boldsymbol{r_{12}}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) \tag{4}$$



We introduce site correlation functions (see picturE):

$$g_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) = N(N-1)\frac{\Omega}{\rho^2} \int \delta(\boldsymbol{R_1})\delta(\boldsymbol{R_2}+\boldsymbol{r_{c_2\beta}}-\boldsymbol{r_\beta}-\boldsymbol{R_1}) P(\boldsymbol{R_1}, \boldsymbol{R_2}, \boldsymbol{r^{N-2}}, \boldsymbol{\omega}^{N-2}) d\boldsymbol{R_1} d\boldsymbol{R_2} d\boldsymbol{\omega_2} d\boldsymbol{r}^{N-2} d\boldsymbol{\omega}^{N-2} \tag{5}$$

The delta function yields $\boldsymbol{R_1} = 0$ and kills integral over $\boldsymbol{R_1}$:

$$g_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) = \frac{\Omega}{\rho^2} \int \delta(\boldsymbol{R_2} + r_{c_2\beta} - r_\beta) N(N-1) P(\boldsymbol{0}, \boldsymbol{R_2}, \boldsymbol{r^{N-2}}, \boldsymbol{\omega}^{N-2}) d\boldsymbol{R_2} d\boldsymbol{\omega_2} d\boldsymbol{r}^{N-2} d\boldsymbol{\omega}^{N-2} \quad (6)$$

Becasue of homogenity:

$$\int P(\boldsymbol{0}, \boldsymbol{R_2}, \boldsymbol{r^{N-2}}, \boldsymbol{\omega}^{N-2}) d\boldsymbol{R_1} = \int P(\boldsymbol{R_1}, \boldsymbol{R_2}, \boldsymbol{r^{N-2}}, \boldsymbol{\omega}^{N-2}) d\boldsymbol{R_1} = V \quad (7)$$

Thus We may add one more integral to the expression (6): we need only divide one more time by V:

$$g_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) = \frac{\Omega}{\rho^2 V} \int \delta(\boldsymbol{R_2} + r_{c_2\beta} - r_\beta) N(N-1) P(\boldsymbol{R_1}, \boldsymbol{R_2}, \boldsymbol{r^{N-2}}, \boldsymbol{\omega}^{N-2}) d\boldsymbol{R_1} d\boldsymbol{R_2} d\boldsymbol{\omega_2} d\boldsymbol{r}^{N-2} d\boldsymbol{\omega}^{N-2} \quad (8)$$

Using the definitions (1)(4) we have:

$$N(N-1) \int P(\boldsymbol{R_1}, \boldsymbol{R_2}, \boldsymbol{\omega}^N) d\boldsymbol{r}^{N-2} d\boldsymbol{\omega}^{N-2} = \frac{\rho^2}{\Omega^2} g(\boldsymbol{r_{12}}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) \quad (9)$$

Also, in our case $\boldsymbol{R_1} = 0$ and $\boldsymbol{r_{12}} = \boldsymbol{R_2}$. The integration over R_1 gives the volume V We have

$$g_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) = \frac{1}{\Omega} \int \delta(\boldsymbol{R_2} + r_{c_2\beta} - r_\beta) g(\boldsymbol{R_2}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) d\boldsymbol{R_2} d\boldsymbol{\omega_2} \quad (10)$$

Let's find the fourier transform of g_β. To avoid thinking much, we do'nt calculate the pre-factor of Fourier integral and call it K_{FT}

$$\hat{g}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) = \frac{1}{\Omega} K_{FT} \int \int d\boldsymbol{r_\beta} e^{i\boldsymbol{k}\boldsymbol{r_\beta}} \delta(\boldsymbol{R_2} + \boldsymbol{r_{c_2\beta}} - \boldsymbol{r_\beta}) g(\boldsymbol{R_2}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) d\boldsymbol{R_2} d\boldsymbol{\omega_2} \quad (11)$$

The delta function kill the integral and gives $\boldsymbol{r_\beta} = \boldsymbol{R_2} + \boldsymbol{r_{c_2\beta}}$:

$$\hat{g}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) = \frac{1}{\Omega} K_{FT} \int e^{i\boldsymbol{k}(\boldsymbol{R_2} + \boldsymbol{r_{c_2\beta}})} g(\boldsymbol{R_2}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) d\boldsymbol{R_2} d\boldsymbol{\omega_2}$$

$$= \frac{1}{\Omega} \int e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} K_{FT} \int g(\boldsymbol{R_2}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) e^{i\boldsymbol{k}\boldsymbol{R_2}} d\boldsymbol{R_2} d\boldsymbol{\omega_2} \quad (12)$$

Inner integral gives the Fourier transform of g:

$$\hat{g}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) = \frac{1}{\Omega} \int e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} \hat{g}(\mathbf{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) d\boldsymbol{\omega_2} \quad (13)$$

The site total correlation function is defined as:

$$h_\beta(\boldsymbol{r}_\beta, \omega_1) = g_\beta(\boldsymbol{r}_\beta, \omega_1) - 1 \quad (14)$$

Let's look at the fourier transform of unity

$$\hat{1} = K_{FT} \int e^{i\boldsymbol{k}\boldsymbol{r}} d\boldsymbol{r} = K_{FT} \int e^{i\boldsymbol{k}\boldsymbol{r} + i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} d\boldsymbol{r} = e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} \hat{1} \quad (15)$$

Lokking at the Fourier transforom of h_β:

$$\hat{h}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) = \hat{g}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) - \hat{1} = \frac{1}{\Omega} \int e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} \hat{g}(\mathbf{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) d\boldsymbol{\omega_2} - e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} \hat{1}$$

$$= \frac{1}{\Omega} \int e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} (\hat{g}(\mathbf{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) - \hat{1}) d\boldsymbol{\omega_2} = \frac{1}{\Omega} \int e^{i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} \hat{h}(\mathbf{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) d\boldsymbol{\omega_2} \quad (16)$$

0.2 c function

We assume, that

$$c(\boldsymbol{r}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) = \sum_{\beta} c_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) \tag{17}$$

Taking Fourier transform we have (remember from picturE: $\boldsymbol{r_\beta} = \boldsymbol{r_{12}} + \boldsymbol{r_{c_2\beta}}$)

$$\hat{c}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) = K_{FT} \sum_{\beta} \int e^{i\boldsymbol{k}\boldsymbol{r_{12}}} c_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) =$$

$$K_{FT} \sum_{\beta} \int e^{i\boldsymbol{k}\boldsymbol{r_\beta} - i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} c_\beta(\boldsymbol{r_\beta}, \boldsymbol{\omega_1}) = \sum_{\beta} \int e^{-i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) \tag{18}$$

The OZ equation in Fourier space:

$$\hat{h}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) = \hat{c}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) + \frac{\rho}{\Omega} \int \hat{h}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_3}) \hat{c}(\boldsymbol{k}, \boldsymbol{\omega_3}, \boldsymbol{\omega_2}) d\boldsymbol{\omega}_3 \tag{19}$$

Putting here (18):

$$\hat{h}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_2}) = \sum_{\beta} \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1},) e^{-i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} + \frac{\rho}{\Omega} \sum_{\beta} \int \hat{h}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_3}) \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1},) e^{-i\boldsymbol{k}\boldsymbol{r_{c_2\beta}}} d\boldsymbol{\omega}_3 \tag{20}$$

We multiply both parts by $e^{i\boldsymbol{k}\boldsymbol{r_{c_2\alpha}}}$ and take integral $\frac{1}{\Omega}\int < \cdot > d\omega_2$. In the left side the definition (16) appear:

$$\begin{aligned} \hat{h}_\alpha(\boldsymbol{k}, \boldsymbol{\omega_1}) = \textstyle\sum_\beta \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) \cdot \frac{1}{\Omega} \int e^{-i\boldsymbol{k}\boldsymbol{r_{c_2\beta}} + i\boldsymbol{k}\boldsymbol{r_{c_2\alpha}}} d\boldsymbol{\omega}_2 + \\ \frac{\rho}{\Omega} \textstyle\sum_\beta \int \hat{h}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_3}) \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) \frac{1}{\Omega} \int e^{-i\boldsymbol{k}\boldsymbol{r_{c_2\beta}} + i\boldsymbol{k}\boldsymbol{r_{c_2\alpha}}} d\boldsymbol{\omega}_2 d\boldsymbol{\omega}_3 \end{aligned} \tag{21}$$

We define

$$w_{\alpha\beta}(\boldsymbol{k}, \boldsymbol{\omega_1}) = \frac{1}{\Omega} \int e^{-i\boldsymbol{k}\boldsymbol{r_{c_2\beta}} + i\boldsymbol{k}\boldsymbol{r_{c_2\alpha}}} d\boldsymbol{\omega}_2 \tag{22}$$

And have:

$$\hat{h}_\alpha(\boldsymbol{k}, \boldsymbol{\omega_1}) = \textstyle\sum_\beta \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) w_{\alpha\beta} + \frac{\rho}{\Omega} \sum_\beta \int \hat{h}(\boldsymbol{k}, \boldsymbol{\omega_1}, \boldsymbol{\omega_3}) \hat{c}_\beta(\boldsymbol{k}, \boldsymbol{\omega_1}) w_{\alpha\beta} \omega_3 \tag{23}$$

We may put here recursively the definition of h from (20). We obtain chain

$$h_\alpha(\mathbf{k}, \omega_1) = \sum_{\beta} \hat{c}_\beta(\mathbf{k}, \omega_1) \hat{\omega}_{\beta\alpha}(k) + \rho \sum_{\gamma,\beta} \langle \hat{c}_\gamma(\mathbf{k}, \omega_1) e^{-i\mathbf{k}\cdot\mathbf{r}_{c3\gamma}} \hat{c}_\beta(\mathbf{k}, \omega_3) \hat{\omega}_{\beta\alpha}(k) \rangle_{\omega_3}$$

$$+ \rho^2 \sum_{\lambda,\gamma,\beta} \langle \hat{c}_\lambda(\mathbf{k}, \omega_1) e^{-i\mathbf{k}\cdot\mathbf{r}_{c4\lambda}} \hat{c}_\gamma(\mathbf{k}, \omega_4) e^{-i\mathbf{k}\cdot\mathbf{r}_{c3\gamma}} \hat{c}_\beta(\mathbf{k}, \omega_3) \hat{\omega}_{\beta\alpha}(k) \rangle_{\omega_4\omega_3} + \cdots .$$

We define the site-site direct correlation functions as:

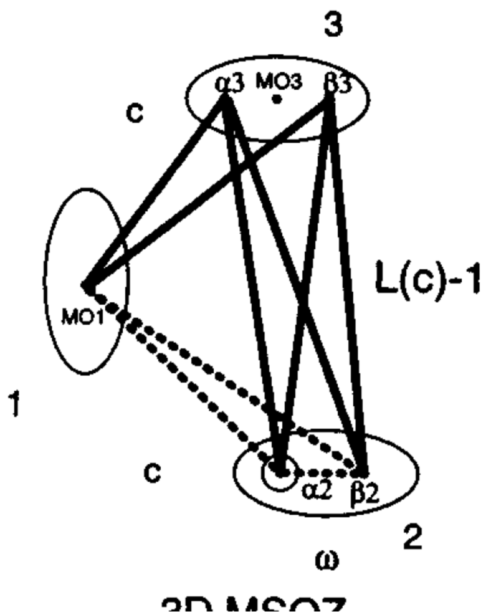
$$\tilde{c}_{\beta\gamma}(\mathbf{k}) = \frac{1}{\Omega} \int e^{-i\boldsymbol{k}\boldsymbol{r_{c_3\gamma}}} c_\beta(\boldsymbol{k}, \omega_3) d\boldsymbol{\omega}_3 \tag{24}$$

(Just for note: $e^{-i\boldsymbol{k}\boldsymbol{r_{c_3\gamma}}}$ is Fourier transform of delta function)

Let we have K sites in the solvent molecule. We may put solute-solvent site correlation functions h_α, c_α into the vectors $\mathbf{h}, \mathbf{c}$ of size $K \times 1$. We may put the site-site direct correlation functions and intramolecular correlation functions $w_{\alpha\beta}$ into the matrices $\mathbf{C}, \mathbf{W}$ of size $K \times K$.

The summations become the matrix multiplications, the chain is written as:

$$\mathbf{h} = \mathbf{W}\mathbf{c} + \mathbf{W}\rho\mathbf{C}\mathbf{c} + \mathbf{W}\rho^2\mathbf{C}^2\mathbf{c} + \cdots = \mathbf{W}\left(\rho\mathbf{C} + (\rho\mathbf{C})^2 + \cdots\right)\mathbf{c} \tag{25}$$



Using the formula for the sum of the geometric progression for the sum of matrices in brackets, we write:

$$\mathbf{h} = \mathbf{W}\left(1 - \rho\mathbf{C}\right)^{-1}\mathbf{c} \tag{26}$$

This is 3D-RISM equation in Fourier space. If one wants very much, he may perform an Inverse Fourier transform and obtain the set of 3D-RISM equations in real space (however i don't know what for...)

In the 3D RISM, only the solute molecule is treated on a molecular level. All solvent molecules are the same as in usual RISM.